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EP-A-0 000 282
GB-A-2 034 300

CHEMICAL ABSTRACTS, vol. 93, no. 22, December 1980, pages 291,292, no. 209118j, Columbus Ohio (USA);

PHYSICS AND CHEMISTRY OF GLASS, vol. 19, no. 1, February 1978, pages 1-4; A.G. DUNN et al.: "Near infrared optical absorption of iron (II) in some sodium borosilicate glasses"

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Description

The present invention relates to a glass suitable for use in the cores of optical fibres, especially for use as core glasses in the production of step-index high numerical aperture (NA) optical fibres, most especially by the double crucible process. The present invention further relates to methods of making such compositions and to optical fibres containing them.

High NA optical fibres are particularly useful for short optical fibre links (e.g. of length less than 1 km) where efficient power launching is of considerable importance. Among such short links are data links between computers and ancillary equipment and also links in telephone exchanges.

In order to facilitate coupling to other system components such fibres may be required to have large core diameters of for example 175 μm and, moreover, to have an acceptable level of loss. As the optical fibres are principally intended to be utilised over relatively short links losses of up to 10 dB/km or in some cases more (e.g. up to 15 or 20 dB/km) are acceptable, although it is clearly desirable to reduce the loss as much as possible within the constraints.

The numerical aperture of a fibre is theoretically equal to

$$\sqrt{n_1^2 - n_2^2}$$

where n_1 is the refractive index of the core and n_2 is the refractive index of the cladding. The amount of light coupled into an optical fibre, other things being equal, is usually proportional to the product of the square of the numerical aperture and the cross-sectional area of the fibre core.

In our European patent application 0018110A, we described, *inter alia*, core glasses suitable for use in optical fibres which had refractive indices in the range from 1.540 to 1.610, were not subject to devitrification or phase separation, and which contained the five components Na_2O (soda or sodium oxide), B_2O_3 (boric oxide), BaO (baria or barium oxide), SiO_2 (silica or silicon dioxide), and GeO_2 (germania or germanium dioxide) and only small amounts of other components. Both barium oxide and germanium dioxide are highly refractive components in sodium borosilicate glasses, i.e. their presence raises the refractive index of the glass. In order to minimise loss in the eventual fibre, it was necessary to use intermediate reducing conditions in the production of these glasses, these conditions corresponding to a partial pressure of oxygen of about 10^{-6} atmospheres. More oxidising conditions than this led to increased loss through absorption by transition metal impurities such as copper while more reducing conditions (e.g. corresponding to a partial oxygen pressure of 10^{-13} atmospheres) led to a very high scatter loss from unknown causes.

The Na_2O:B_2O_3 molar ratio in these glasses was high (substantially in excess of 2:1).

The use of these glasses to produce fibres by the double crucible process was also described.

In European patent application A—000282, a glass comprising Na_2O, B_2O_3 BaO (or CaO) and SiO_2, but not ZrO_2, is disclosed. The composition of the glass is such that it is not subject to devitrification or phase separation during optical fibre production. A method of preparing the glass is also disclosed which comprises the steps of preparing a melt (including about 0.1 mole per cent of Al_2O_3 as a redox buffering oxide) and bubbling a mixture of carbon monoxide and carbon dioxide through the molten glass.

The use of ZrO_2 (zirconia or zirconium dioxide) as a highly refractive component in vitreous silica for optical fibres is known from our UK patent 1 368 093.

M Yoshiyagawa, Y Kaite, T Ikuma and T Kishimoto, J Non-Crystalline Solids, 40, 489—497 (1980) refers to the use, alone or in combination, of a range of oxides in sodium borosilicate glasses for optical fibres. These oxides are MgO, CaO, SrO, BaO, ZnO, Al_2O_3, La_2O_3, TiO_2, GeO_2 and ZrO_2. No preference among these oxides is stated and detailed compositions are not specified.

In Chemical Abstract No. 93:209118j (1980) and Japanese unexamined patent application 80 60040 there are described sodium borosilicate glasses containing barium oxide and zirconium dioxide but these have very high barium oxide contents and very high refractive indexes ranging from 1.58 to 1.65. The same document also discloses glasses containing substantial quantities of further components in combination and not in combination with BaO and ZrO_2. Oxides whose uses are suggested and exemplified are Li_2O, K_2O, Rb_2O, Cs_2O, MgO, CaO, SrO, ZnO, Al_2O, La_2O_3, TiO_2, and GeO_2.

In US patent 4 265 667 (equivalent to French published patent specification 2 481 261) there are described various stable sodium borosilicate glasses containing BaO and ZrO_2. These have very high BaO contents, have refractive indexes in excess of 1.61, and contain further components, for example Li_2O, K_2O, Rb_2O, Cs_2O, MgO, CaO, SrO, ZnO, Al_2O_3, La_2O_3, TiO_2 and GeO_2.

In French patent application 2 438 018 (equivalent to UK patent application 2 034 300) there are disclosed sodium borosilicate glasses containing BaO and ZrO_2 which have refractive indexes of less than 1.540. There is additionally a disclosure of a glass of refractive index exceeding 1.61 similar to those described in Chemical Abstracts No. 93: 209 118j and already referred to. In the said French patent application, the use is suggested and exemplified also of further components in combination with and not in combination with BaO and ZrO_2. Such components are Li_2O, K_2O, Cs_2O, Tl_2O, MgO, CaO, ZnO, PbO, ZnO, Al_2O_3, and TiO_2. The main concern of the French patent application is the production of cladding glasses where water resistance is a prime consideration.

The present invention is based on our surprising discovery that satisfactory glasses

having refractive indexes in the range 1.540 to 1.610 (but having advantages over the similar glasses of European patent 0018110A) can be produced by the use as components of Na_2O, B_2O_3, BaO, SiO_2, and ZrO_2 with only minor quantities of other components, the components being used in proportions quite dissimilar from the glasses of the aforesaid prior art on BaO- and ZrO_2- containing sodium borosilicate glasses. From the aforesaid prior art on BaO- and ZrO_2-containing sodium borosilicate glasses it could not have been predicted that the glasses provided by the present invention would be satisfactory, since it is well known in this field that substantial variations of composition from known satisfactory compositions can affect stability of a glass and the optical losses in the glass. (In this respect, and generally, it may be noted that glasses which are apparently stable but have compositions close to unstable ones, frequently yield fibres having high loss).

The present invention provides a glass suitable for use in the core of an optical fibre and having a composition such that it is not subject to devitrification or phase separation, which glass

(I) has a refractive index in the range from 1.540 to 1.610 and

(II) comprises the five components Na_2O, B_2O_3, BaO, SiO_2, and a highly refractive component other than BaO and not more than 5 weight per cent of any further components taken together relative to the said five components taken together, the proportion of BaO being in the range from 2 to 12 mole per cent relative to the said five components taken together and the proportion of SiO_2 being in the range from 40 to 63 mole per cent relative to the said five components taken together,

characterised in that

(i) the said highly refractive component is ZrO_2 in a proportion lying in the range from 1.5 to 15 mole per cent relative to the said five components taken together, the proportion of SiO_2 and ZrO_2 taken together being not more than 65 mole per cent relative to the said five components taken together, and

(ii) the $Na_2O:B_2O_3$ molar ratio is in the range from 1.1:1 to 1.6:1.

An advantage of these glasses over the aforesaid glasses of European patent application 0018110A is that they do not display scatter loss when highly reduced. This permits the best possible suppression of absorption loss due to transition metal ions such as copper by a convenient process.

A further advantage is that the amount of ZrO_2 required to achieve a given refractive index is less than the amount of GaO_2, so that the purity specification for the ZrO_2 need not be so stringent for a given maximum prescribed level of interfering impurities. There are additionally overall cost advantages to the use of ZrO_2 of the requisite purity in the requisite quantities. Cost advantages are especially important for large diameter cores because of the amount of material involved.

The glasses according to the present invention are generally more viscous when molten than the aforesaid glasses of European patent application 0018110A, which offers interesting new possibilities. In particular, it offers a way of avoiding or reducing the problem that can be encountered with these prior art glasses, namely the excessively rapid pulling of core glass compared with the cladding glass in the double crucible process.

On the various compositional features of the glass according to the present invention further observations may be made as follows, without explicit comparison with the prior art.

The limit of 5 weight per cent on further components reflects the fact that (apart from possibly redox buffering agents) other components can usually be avoided. This is good because, firstly, the use of numerous components raises the possibly expensive question of the purity specification with each one and, secondly it simplifies production of the glass. Apart from redox buffering agents, a minor component which we presently think may prove attractive is Al_2O_3, perhaps at a level of 1 to 3 weight per cent.

The lower limit on the proportion of ZrO_2 ensures that at least a part of the refractive index increase is due to zirconia. With BaO alone, it is difficult to achieve refractive indices much in excess of 1.55 without the glass becoming unstable. However, even with the use of ZrO_2 a molar proportion in excess of 15 per cent tends to lead to instability (albeit for a much higher refractive index).

The range for molar ratio $Na_2O:B_2O_3$ is especially suitable in achieving a good balance between glass stability (favoured by Na_2O) and fibre-forming performance in the double crucible process (favoured by B_2O_3).

Preferably, the proportion of ZrO_2 in the present invention is in the range from 3 to 10 mole per cent. Preferably, the proportion of BaO is in the range from 4 to 10 mole per cent.

The molar ratio $Na_2O:B_2O_3$ is preferably in the range 1.10 to 1.50, especially from 1.10 to 1.40.

The present invention affords glasses with especially good viscosity properties for the range of refractive index 1.550 to 1.590.

Preferably the proportion of Na_2O lies in the range from 15 to 25 mole per cent and that of B_2O_3 lies in the range from 10 to 20 mole per cent, both proportions being relative to the five components (Na_2O, B_2O_3, BaO, SiO_2, and ZrO_2) taken together. Preferably, the proportion of SiO_2 and ZrO_2 taken together is at least 50 mole per cent relative to the said five components taken together, and more preferably at least 55 mole per cent.

It will be appreciated that the glass according to the present invention can be formed in any appropriate manner, and that formation as a melt which can be subsequently converted to a solid glass for storage is especially convenient.

The present invention further provides a method of preparing the glass provided by the invention which comprises the steps of

(a) preparing a melt including from 0.01 to 1 weight per cent of a redox buffering agent or of one or more redox buffering agents taken together relative to the said five components taken together, and

(b) passing carbon monoxide through the melt.

We find arsenic trioxide, As_2O_3, to be a convenient redox buffering agent, but other oxides, for example antimony oxide (Sb_2O_3), can also be used. Preferably, the amount employed lies in the range 0.05 to 0.2 weight per cent. The function of these agents is described in general terms in European patent application 0019110A and in UK patent 1 507 711 referred to therein.

In general, melt composition and final glass composition are practically the same, and any deviations can be allowed for after simple trial and error. We have observed minor deviations due to reduction of As_2O_3 to volatile As during step (b).

Carbon monoxide is conveniently used in the form of a mixture with carbon dioxide, said mixture however preferably not containing less than 10 per cent by volume of carbon monoxide.

Depending on the transition metal contaminents in the melt, it may be desirable to pass oxygen through the melt (either pure or in admixture with other gases) prior to step (b).

The present invention also provides an optical fibre comprising a core comprising the glass provided by the present invention and a cladding comprising a sodium borosilicate glass of lower refractive index.

The sodium borosilicate glass used for the cladding may include components other than Na_2O, B_2O_3, and SiO_2. Preferably, only small quantities of such further components are used, e.g. Al_2O_3 at a level of 1—2 mole per cent relative to Na_2O, B_2O_3, SiO_2, and Al_2O_3 taken together may afford advantages of durability and water resistance. Preferably, the glass is in a highly reduced state.

Preferred fibres in accordance with the present invention are made by the double crucible process. Convenient large core high NA fibres in accordance with the present invention have a core diameter in the range from 90 to 220 µm. The outer diameter of the cladding is normally at least 25 µm greater than the core diameter and is conveniently in the range from 115 µ to 270 µm.

The present invention will now be further illustrated by means of Examples 1 to 12 and Comparative Examples C1 to C5 (not in accordance with the invention).

Each of these Examples and Comparative Examples illustrates a core glass material (or an attempted core glass material). The compositions and observed properties are given in Tables 1 and 2 respectively.

TABLE 1
Glass compositions

Example No.	Mole percentages				
	Na_2O	B_2O_3	BaO	ZrO_2	SiO_2
1	20	14.5	4	2	59.5
2	20	14.5	4	3.5	58
3	20	14.5	4	5	56.5
4	20	14.5	4	10	51.5
5	20	14.5	4	12.5	49
6	20	14.5	4	15	46.5
C1	20	14.5	4	16	45.5
C2	20	14.5	4	17.5	44
C3	20	16	4	17.5	42.5
7	20	18	4	8	50
8	20	18	4	15	43
9	19	15	8	3	55
10	19	15	8	5.16	52.84
11	19	15	8	7	51
12	19	15	8	10	48
	Na_2O	B_2O_3	BaO	GeO_2	SiO_2
C4	20	8.3	11.7	12	48
C5	20	8.3	11.7	25	35

TABLE 2
Glass properties

Example No.	ρ in g cm^{-3}	α in 10^{-7} °C^{-1}	n_D	Tg in °C	SP in °C	Stability
1	2.73	81.9	1.5438	570	635	Yes
2	2.76	81	1.5509	574	640	Yes
3	2.79	74.8	1.5577	587	660	Yes
4	2.89	76.8	1.5815	592	670	Yes
5	2.94	75.9	1.5915	592	683	Yes
6	2.99	72.5	1.6028	615	672	Yes
C1	—	—	—	—	—	No
C2	—	—	—	—	—	No
C3	—	—	—	—	—	No
7	2.88	88.6	1.5750	575	645	Yes
8	2.97	82.9	1.6017	599	658	Yes
9	2.90	81.1	1.5815	578	620	Yes
10	2.94	79.7	1.5714	575	645	Yes
11	2.98	82.05	1.5794	595	648	Yes
12	3.05	78.1	1.5938	593	643	Yes
C4	3.11	—	1.5698	523	585	Yes
C5	3.34	—	1.5916	505	545	Yes

ρ=density, α=linear coefficient of expansion, n_D=refractive index (NaD line), Tg=glass temperature, SP=dilatometric softening point.

The preparative procedure for Examples 1 to 12 and Comparative Examples C1 to C3 was as follows: The starting materials were high-purity Na_2CO_3, $Na_2B_4O_7$, $BaCO_3$, ZrO_2, SiO_2, and As_2O_3 powders. The powders were mixed together in the proportions appropriate to the desired glass composition, the As_2O_3 being used at a level of 0.1 weight per cent relative to the other components taken together. The mixture was then introduced gradually into a silica crucible at 1100°C where it melted. The melt was left to react for a further hour or so and the temperature was raised to 1150 to 1200°C and pure dry carbon dioxide was passed over the top of the melt at 2 litre/min, this flow being maintained to the end of the preparation. Gases were bubbled through the melt in the following order: pure dry carbon dioxide for 2 hours; pure dry oxygen for ½ hour; and a mixture of 18 volume per cent carbon monoxide and 82 volume per cent carbon dioxide for 1½ hours. In each case the flow rate was 500 ml/min. Bubbling was then discontinued (the flow of carbon dioxide over the melt being maintained) and the melt was heated to 1250°C for 18 hours to remove bubbles. The melt was then cooled to 850—900°C, and the glass was removed as rods and stored.

The preparative procedure for Comparative Examples C4 and C5 was in accordance with the invention of European patent application 0018110A and in particular the glass was in an intermediate redox state (corresponding to a partial oxygen pressure of about 10^{-6} atmospheres) achieved with the use of pure dry carbon dioxide instead of the carbon monoxide/carbon dioxide mixture (which latter corresponded to a partial oxygen pressure of about 10^{-13} atmospheres).

The three series of Examples 1 to 6, 7 to 8, and 9 to 12 respectively show how, if the molar proportions of Na_2O, B_2O_3, and BaO are fixed, the refractive index varies as one changes the relative amounts of ZrO_2 and SiO_2 constituting the balance of the composition.

The glass of Example 12 was found to corrode the silica crucible in which it was being melted, but this problem is one which may be overcome by the use of an alternative material for the crucible.

Comparative Examples C1 to C3 illustrate the instability (due to crystallization) that arises for high ZrO_2 concentrations. Comparative Examples C4 and C5 illustrate the lower glass and softening temperatures (and hence viscosities) of the prior art glasses in accordance with European patent application 0018110A.

From glasses in accordance with the present invention, fibres were prepared having core diameters of 175 µm and outer cladding diameters of 200 µm. The cladding glasses were prepared with the use of As_2O_3 as a redox buffering agent and with the use of a carbon monoxide/carbon dioxide mixture to achieve a highly reduced state.

An optical fibre was prepared from the glass of Example 2 by the double crucible process. The drawing (i.e. nozzle) temperature was approximately 850°C. The cladding glass had the composition 20 mole % Na_2O, 17.5 mole % B_2O_3, 61 mole % SiO_2, and 1.5 mole % Al_2O_3 and had a refractive index n_D of 1.5185. The numerical aperture of the fibre was 0.32 and the fibre had a loss of 7.3 dB/km at 850 nm.

An optical fibre was prepared also from the glass of Example 7. The drawing temperature was in this case about 900°C because of the higher viscosity of the glass. The cladding glass had the composition 20 mole % Na_2O, 17.5 mole % B_2O_3, 59 mole % SiO_2, 2 mole % MgO, and 1.5 mole % Al_2O_3 and a refractive index of 1.5183. The numerical aperture was 0.41, and the fibre had a loss at 850 nm of 10.9 dB/km.

Claims

1. A glass suitable for use in the core of an optical fibre and having a composition such that it is not subject to devitrification or phase separation, which glass

(i) has a refractive index in the range from 1.540 to 1.610 and

(ii) comprises the five components Na_2O, B_2O_3, BaO, SiO_2, and a highly refractive component other than BaO and not more than 5 weight per cent of any further components taken together relative to the said five components taken together, the proportion of BaO being in the range from 2 to 12 mole per cent relative to the said five components taken together and the proportion of SiO_2 being in the range from 40 to 63 mole per cent relative to the said five components taken together,

characterised in that

(i) the said highly refractive component is ZrO_2 in a proportion lying in the range from 1.5 to 15 mole per cent relative to the said five components taken together, the proportion of SiO_2 and ZrO_2 taken together being not more than 65 mole per cent relative to the said five components taken together, and

(ii) the $Na_2O:B_2O_3$ molar ratio is in the range from 1.1:1 to 1.5:1.

2. A glass according to claim 1 wherein the proportion of ZrO_2 is in the range from 3 to 10 mole per cent.

3. A glass according to claim 1 or claim 2, wherein the proportion of BaO is in the range from 4 to 10 mole per cent.

4. A glass according to any preceding claim, wherein the molar ratio $Na_2O:B_2O_3$ is in the range from 1.10 to 1.40.

5. A glass according to any preceding claim, wherein the proportion of Na_2O is in the range from 15 to 25 mole per cent relative to the said five components taken together.

6. A glass according to any preceding claim, wherein the proportion of B_2O_3 is in the range from 10 to 20 mole per cent relative to the said five components taken together.

7. A glass according to any preceding claim, wherein the proportion of SiO_2 and ZrO_2 taken together is in the range from 50 to 65 mole per cent relative to the said five components taken together.

8. A glass according to claim 7, wherein the proportion of SiO_2 and ZrO_2 taken together is in the range from 55 to 65 mole per cent relative to the said five components taken together.

9. A glass according to any preceding claim which has a refractive index in the range from 1.550 to 1.580.

10. A glass according to any preceding claim which is in a highly reduced state.

11. A method of preparing a glass according to any preceding claim which comprises the steps of

(a) preparing a melt including from 0.01 to 1 weight per cent of a redox buffering agent or of one or more redox buffering agents taken together relative to the said five components taken together, and

(b) passing carbon monoxide through the melt.

12. A method according to claim 11, wherein the redox buffering agent is As_2O_3.

13. A method according to claim 11 or claim 12, wherein the melt of (a) includes from 0.05 to 0.2 weight per cent of a redox buffering agent.

14. A method according to any of claims 11 to 13, wherein step (b) is performed with a mixture of carbon monoxide and carbon dioxide containing at least 10 mole per cent of the former.

15. A method according to any of claims 11 to 14, wherein oxygen is passed through the melt between step (a) and step (b).

16. An optical fibre which comprises a core comprising a glass according to any of claims 1 to 10 or prepared according to any of claims 11 to 15 and a sodium borosilicate cladding glass.

17. An optical fibre according to claim 16, wherein the core diameter is in the range from 50 to 220 µm.

18. An optical fibre according to claim 16 or claim 17, which has a loss at 850 nm of not more than 20 dB/km.

19. An optical fibre according to claim 18, which has a loss at 850 nm of not more than 15 dB/km.

Patentansprüche

1. Zur Verwendung im Kern einer optischen Faser geeignetes Glas mit einer solchen Zusammensetzung, daß es keine Entglasung oder Phasentrennung erleidet, welches Glas

(I) einen Brechungsindex im Bereich von 1,540 bis 1,610 hat und

(II) die fünf Bestandteile Na_2O, B_2O_3, BaO, SiO_2 und einen hochgradig brechenden Bestandteil außer BaO und nicht mehr als insgesamt 5 Gew.% irgendwelcher weiterer Bestandteile, bezogen auf die Gesamtmenge der fünf Bestandteile, aufweist, wobei der BaO-Anteil im Bereich von 2 bis 12 Mol-%, bezogen auf die Gesamtheit der fünf Bestandteile, liegt und der SiO_2-Anteil im Bereich von 40 bis 63 Mol-%, bezogen auf die Gesamtheit der fünf Bestandteile liegt,

dadurch gekennzeichnet, daß

(I) der hochgradig brechende Bestandteil ZrO_2 in einem Anteil ist, der im Bereich von 1,5 bis 15 Mol-%, bezogen auf die Gesamtheit der fünf Bestandteile, liegt, wobei der Anteil von SiO_2 und ZrO_2 zusammen nicht mehr als 65 Mol-%, bezogen auf die Gesamtheit der fünf Bestandteile, ist und

(II) das Na_2O:B_2O_3-Molverhältnis im Bereich von 1,1:1 bis 1,5:1 ist.

2. Glas nach Anspruch 1, worin der ZrO_2-Anteil im Bereich von 3 bis 10 Mol-% ist.

3. Glas nach Anspruch 1 oder Anspruch 2, worin de BaO-Anteil im Bereich von 4 bis 10 Mol-% ist.

4. Glas nach irgendeinem vorstehenden Anspruch, worin das Mol-verhältnis Na_2O:B_2O_3 im Bereich von 1,10 bis 1,40 ist.

5. Glas nach irgendeinem vorstehenden Anspruch, worin der Na_2O-Anteil im Bereich von 15 bis 25 Mol-%, bezogen auf die Gesamtheit der fünf Bestandteile, ist.

6. Glas nach irgendeinem vorstehenden Anspruch, worin der B_2O_3-Anteil im Bereich von 10 bis 20 Mol-%, bezogen auf die Gesamtheit der fünf Bestandteile, ist.

7. Glas nach irgendeinem vorstehenden Anspruch, worin der Anteil von SiO_2 und ZrO_2 zusammen im Bereich von 50 bis 65 Mol-%, bezogen auf die Gesamtheit der fünf Bestandteile, ist.

8. Glas nach Anspruch 7, worin der Anteil von SiO_2 und ZrO_2 zusammen im Bereich von 55 bis 65 Mol-%, bezogen auf die Gesamtheit der fünf Bestandteile, ist.

9. Glas nach irgendeinem vorstehenden Anspruch, das einen Brechungsindex im Bereich von 1,550 bis 1,590 hat.

10. Glas nach irgendeinem vorstehenden Anspruch, das in einem hochgradig reduzierten Zustand ist.

11. Verfahren zum Herstellen eines Glases nach irgendeinem vorstehenden Anspruch, das die Schritte des

a) Herstellens einer Schmelze, die 0,01 bis 1 Gew.% eines Redoxpuffermittels oder eines oder mehrere Redoxpuffermittel insgesamt, bezogen auf die Gesamtmenge der fünf Bestandteile, enthält, und

b) Durchleitens von Kohlenmonoxid durch die Schmelze umfaßt.

12. Verfahren nach Anspruch 11, wobei das Redoxpuffermittel As_2O_3 ist.

13. Verfahren nach Anspruch 11 oder Anspruch 12, wobei die Schmelze von (a) 0,05 bis 0,2 Gew.% eines Redoxpuffermittels enthält.

14. Verfahren nach irgendeinem der Ansprüche 11 bis 13, wobei der Schritt (b) mit einer Mischung von Kohlenmonoxid und Kohlendioxid durchgeführt wird, die wenigstens 10 Mol-% des ersteren enthält.

15. Verfahren nach irgendeinem der Ansprüche 11 bis 14, wobei zwischen dem Schritt (a) und dem Schritt (b) Sauerstoff durch die Schmelze geleitet wird.

16. Optische Faser, die einen Kern mit einem Glas nach irgendeinem der Ansprüche 1 bis 10 oder das nach irgendeinem der Ansprüche 11 bis 15 hergestellt ist, und ein Natriumborsilikatüberzugsglas aufweist.

17. Optische Faser nach Anspruch 16, worin der Kerndurchmesser im Bereich von 90 bis 220 µm ist.

18. Optische Faser nach Anspruch 16 oder Anspruch 17, das einen Verlust bei 850 nm von nicht mehr als 20 dB/hat.

19. Optische Faser nach Anspruch 18, das einen Verlust bei 850 nm von nicht mehr als 15 dB/km hat.

Revendications

1. Un verre adapté à la constitution du coeur d'une fibre optique et ayant une composition telle qu'il ne soit pas sujet à dévitrification ou séparation de phase, verre qui

(I) a un indice de réfraction compris entre 1,540 et 1,610 et

(II) comprend les cinq composants Na_2O, B_2O_3, BaO, SiO_2, et un composant à haut pouvoir refringent autre que BaO et pas plus de 5% en poids de tous autres composants pris dans leur ensemble relativement aux cinq dits composants pris dans leur ensemble, la proportion de BaO étant comprise entre 2 et 12 moles % relativement aux cinq dits composants pris dans leur ensemble et la proportion de SiO_2 étant compris entre 40 et 63 moles % rélativement aux cinq dits composants pris dans leur ensemble,

caractérisé en ce que

(I) ledit composant hautement refringent est ZrO_2 dans une proportion comprise entre 1,5 et 15 moles pour cent relativement aux cinq dits composants pris dans leur ensemble, la proportion de SiO_2 et ZrO_2 pris dans leur ensemble n'étant pas plus grande que 65 moles pour cent relativement aux cinq dits composants pris dans leur ensemble et

(ii) le rapport molaire $Na_2O:B_2O_3$ est compris entre 1,1:1 et 1,5:1.

2. Un verre selon la revendication 1, caractérisé en ce que la proportion de ZrO_2 est comprise entre 3 à 10 moles pour cent.

3. Un verre selon la revendication 1 ou 2, caractérisé en ce que le BaO est compris entre 4 et 10 moles pour cent.

4. Un verre selon l'une quelconque des revendications précédentes, caractérisé en ce que le rapport molaire $Na_2O:B_2O_3$ est compris entre 1,10 et 1,40.

5. Un verre selon l'une quelconque des revendications précédentes, caractérisé en ce que la proportion de Na_2O est comprise entre 15 et 25 moles pour cent relativement aux cinq dits composants pris dans leur ensemble.

6. Un verre selon l'une quelconque des revendications précédentes, caractérisé en ce que la proportion de B_2O_3 est comprise entre 10 et 20 moles pour cent relativement aux cinq dits composants pris dans leur ensemble.

7. Un verre selon l'une quelconque des revendications précédentes, caractérisé en ce que la proportion de SiO_2 et ZrO_2 pris dans leur ensemble est comprise entre 50 et 65 moles pour cent relativement aux cinq dits composants pris dans leur ensemble.

8. Un verre selon la revendication 7, caractérisé en ce que la proportion de SiO_2 et ZrO_2 pris ensemble est comprise entre 55 et 65 moles pour cent relativement aux cinq dits composants pris dans leur ensemble.

9. Un verre selon l'une quelconque des revendications précédentes, ayant un indice de réfraction compris entre 1,550 et 1,590.

10. Un verre selon l'une quelconque des revendications précédentes, qui est dans un état hautement réduit.

11. Une méthode de préparation d'une verre selon l'une quelconque des revendications précédentes qui comprend les étapes suivantes

(a) préparation d'un bain de fusion comprenant entre 0,01 à 1% en poids d'un agent jouant le rôle de tampon dans la réaction d'oxydo-réduction ou de l'un ou plusieurs agents jouant le rôle de tampon dans la réaction d'oxydo-réduction pris dans leur ensemble relativement aux cinq dits composants pris dans leur ensemble, et

(b) circulation de monoxyde de carbone au travers dudit bain de fusion.

12. Une méthode selon la revendication 11, caractérisé en ce que l'agent jouant le rôle de tampon dans la réaction d'oxydo-réduction est As_2O_3.

13. Une méthode selon la revendication 11 ou 12, caractérisé en ce que le bain de fusion de (a) comprend de 0.05 à 0.2 % en poids le l'agent jouant le rôle de tampon dans la réaction d'oxydo-réduction.

14. Une méthode selon l'une des revendications 11 à 13, caractérisé en ce que l'étape (b) est réalisée en utilisant un mélange de monoxyde de carbone et de dioxyde de carbone contenant au moins 10 moles % de monoxyde de carbone.

15. Une méthode selon l'une quelconque des revendications 11 à 14, caractérisé en ce que de l'oxygène est envoyé à travers le bain en fusion entre l'étape (a) et l'étape (b).

16. Une fibre optique qui comprend un coeur contenant un verre, caractérisé par l'une quelconque des revendications 1 à 10 ou préparé suivant l'une quelconque des revendications 11 à 15 et une enveloppe de verre en borosilicate de sodium.

17. Une fibre optique selon la revendication 16, caractérisé en ce que le diamètre de coeur est compris entre 50 et 220 µm.

18. Une fibre optique selon la revendication 16 ou 17, caractérisé en ce qu'elle a des pertes à 850 nm inférieures à 20 dB/km.

19. Une fibre optique selon la revendication 18, caractérisé en ce qu'elle a des pertes à 850 nm inférieures à 15 dB/km.